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(54) **PREPARATION OF CIGS ABSORBER LAYERS USING COATED SEMICONDUCTOR NANOPARTICLE AND NANOWIRE NETWORKS**

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C09D 11/02 (2014.01)

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CPC **H01L 31/18** (2013.01); **H01L 31/0322** (2013.01); **C09D 11/02** (2013.01); **Y02E 10/541** (2013.01); **Y02E 10/544** (2013.01)

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See application file for complete search history.

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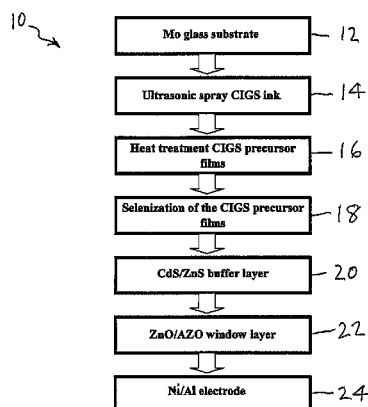
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ABSTRACT

A method of preparing Cu(In,Ga)SSe₂ Cu(In,Ga) (S,Se)₂ (CIGSS) absorber layers uses coated semiconductor nanoparticle and nanowire networks. The nanoparticles and nanowires containing one or more elements from group IB and/or IIIA and/or VIA are prepared from metal salts such as metal chloride and acetate at room temperature without inert gas protection. A uniform and non-aggregation CIGS precursor layer is fabricated with the formation of nanoparticle and nanowire networks utilizing ultrasonic spaying technique. High quality CIGSS film is obtained by cleaning the residue salts and carbon agents at an increased temperature and selenizing the pretreated precursor layer.

14 Claims, 8 Drawing Sheets



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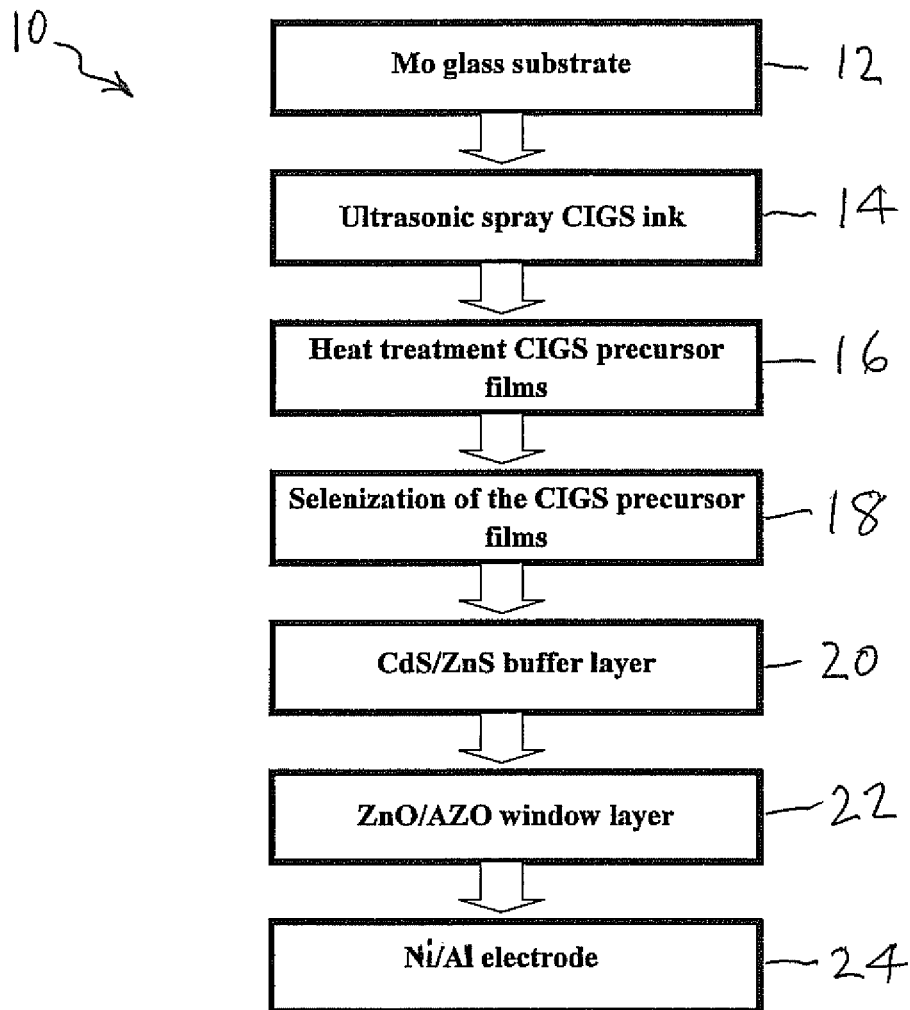


FIG. 1

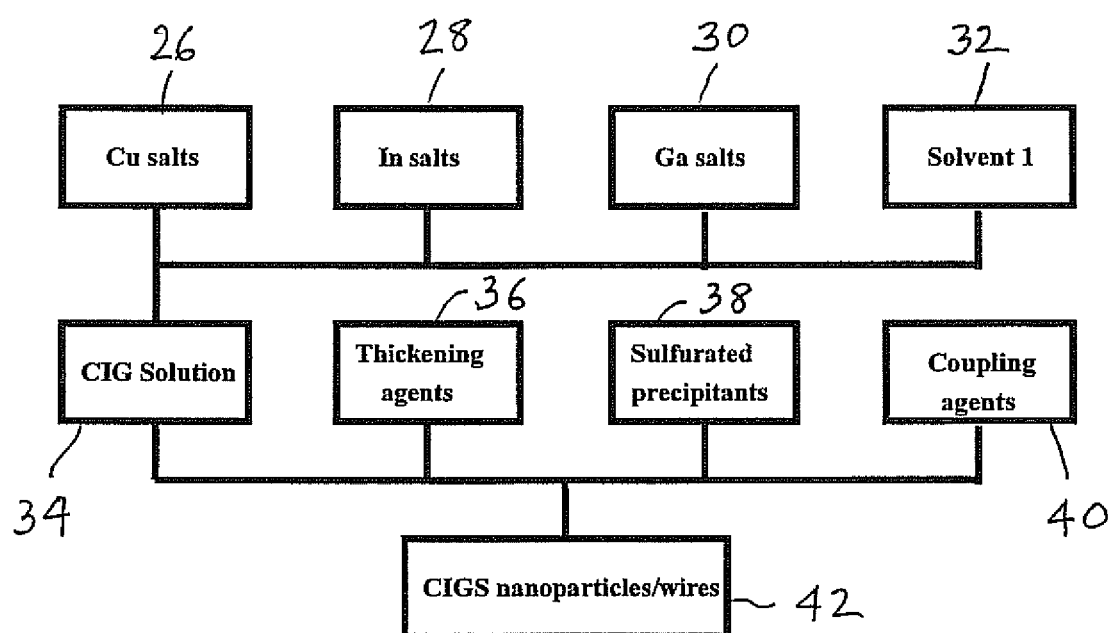


FIG. 2

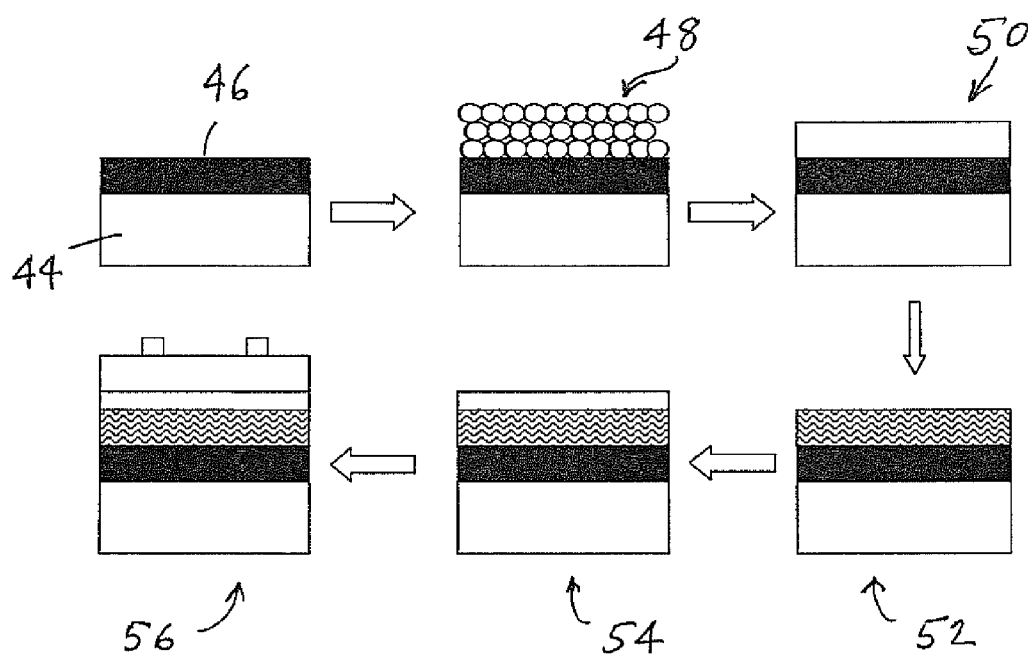


FIG. 3

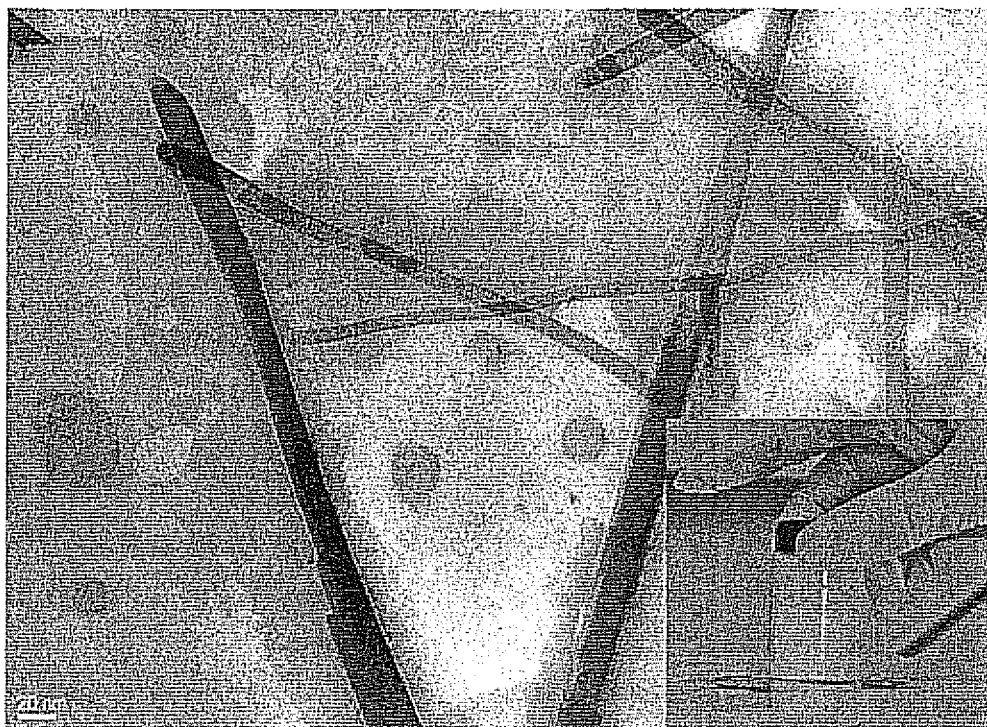


FIG. 4

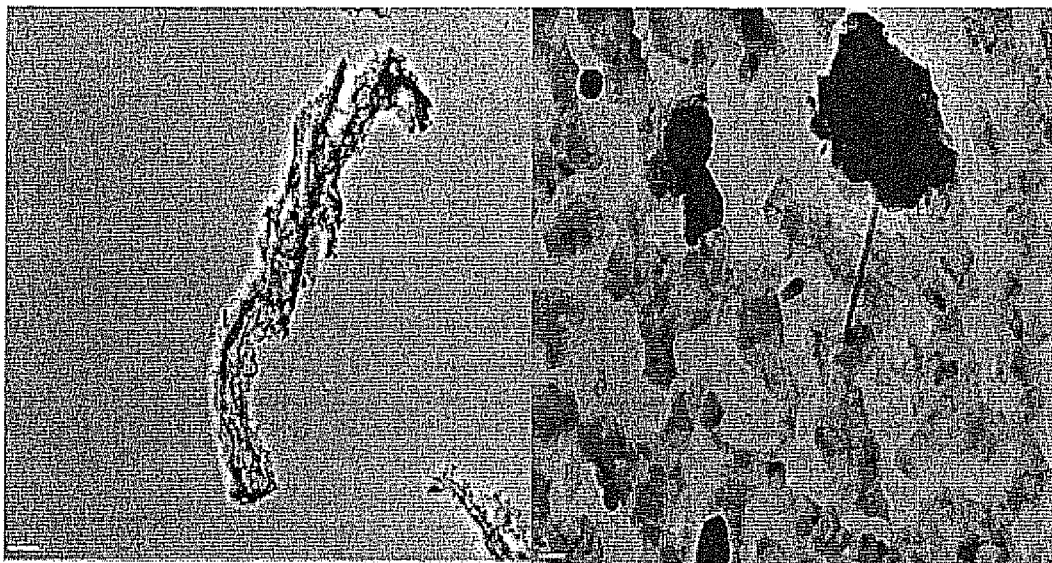


FIG. 5

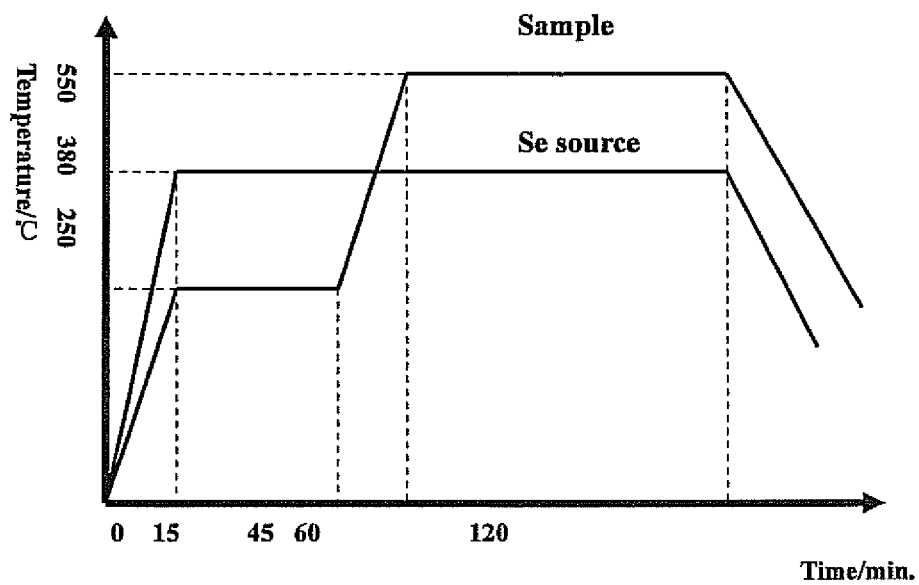


FIG. 6



FIG. 7

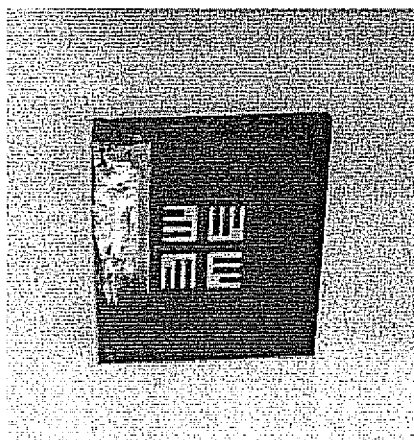
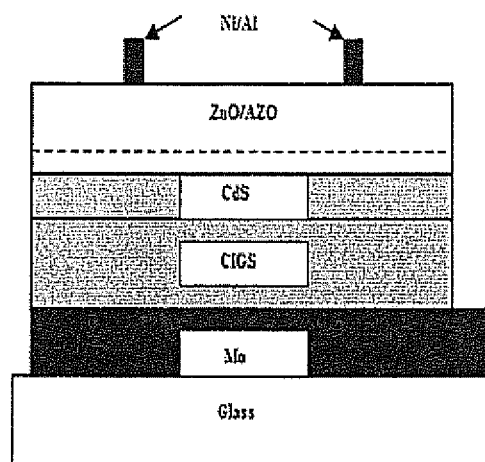


FIG. 8

PREPARATION OF CIGS ABSORBER LAYERS USING COATED SEMICONDUCTOR NANOPARTICLE AND NANOWIRE NETWORKS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a method synthesizing Cu(In,Ga)S₂ nanoparticles/wires based on metal salts.

2. Description of the Prior Art

A CIGS thin film is prepared by the formation of semiconductor nanoparticle and nanowire networks and selenization for a light absorption layer of photovoltaic devices.

Chalcopyrite CuInGaSe₂ CIGSe is a direct band gap semiconductor and has an exceptionally high absorption coefficient of more than 10⁵/cm for 1.5 eV and higher energy photons. According to the recent report from the ZSW, a solar cell based on CIGSe has reached a power conversion efficiency of 20.3%, which is comparable with the energy conversion efficiency of crystalline Si solar cells. Decent conversion efficiency and high chemical stability of CIGSe make itself a promising p-type material for thin film photovoltaic devices.

Vacuum and non-vacuum technologies are the two main methods of preparing CIGSe thin films. Vacuum-based processes including co-evaporation and sputtering, which have been successfully applied in commercial production lines. However, the high cost and complexity of vacuum-based fabrication process become barriers to affordable commercial modules.

An efficient non-vacuum printing process has the potential to overcome this barrier. The low cost technique is inherently suitable for large-scale applications and may benefit from established industries of coatings, paints, inks, electronic ceramics and colloidal systems. In particular, deposition at atmospheric environment offers an opportunity for the deposition of absorber materials at large scale with high throughput. This provides a potential cost advantage over conventional fabrication process that involves expensive vacuum equipment.

Kapur et al (U.S. Pat. No. 6,127,202) describe a method for fabricating a CIGSe solar cell based upon the solution-based deposition of a source material comprised of mechanically milled, oxide-containing, sub-micron sized particles, while Eberspacher and Pauls (U.S. Pat. No. 6,268,014); Published U.S. Patent Application No. 2002/0006470) describe the forming of mixed metal oxide, sub-micron sized particles by pyrolyzing droplets of a solution, then ultrasonically spraying the resulting particles onto a substrate. However, the high-temperature hydrogen reduction step is potentially explosive and requires substantial time and energy. Meanwhile, highly toxic H₂Se gas atmosphere is requested in the selenization process. Byoung Koun Min in Published U.S. Patent Application No. 2012/0080091 A1 also involves the reduction process.

Fuqiang Huang in Published U.S. Patent Application No. 2011/0008927 A1 gets a 14.6% high efficiency employing a non-vacuum liquid-phase chemical technique.

David B. Mitzi. in Published U.S. Patent Application No. 2009/0145482 also gets above 10% efficiency CIGSe thin film solar cells using hydrazine as the solvent source.

Nanosolar Inc. in Published U.S. Patent Application No. 2008/0149176 has used binary copper selenide and indium/gallium selenides nanoparticles as starting materials to fabricate 14% thin film CIGSe solar cells. Single metallic nanoparticles are the simplest form one could design. The

structure of nanoparticles used by Nanosolar has a core-shell structure. Copper nanoparticles serve as the cores which are coated with IIIA-VIA shells such as indium selenide, gallium selenide etc. These selenide nanoparticles are dispersed in organic solution which may contain various ingredients including solvents, surfactants, binders, emulsifiers, thickening agents, film conditioners, anti-oxidants, flow and leveling agents, plasticizers and preservatives. By using the similar core shell strategy, Yoon et al. synthesized CuSe/InSe nanoparticles which yield only ~1% efficiency.

However, those methods mentioned here require toxic reagents, need inert gas protection, require complex processes and are not easy to scale up to mass production. Thus, there is a need in the art, for a non-oxide, nanoparticle based precursor material that overcomes the above disadvantages.

SUMMARY OF THE INVENTION

In order to solve these problems, the subject invention presents a facile way to synthesize soluble CIGS nanoparticles/wires at room temperature under non-vacuum condition and the reaction can finish in 5 minutes. We employ ultrasonic spray to effectively reduce the aggregation and obtain uniform CIGS precursor films. After heat treatment and selenization, high quality Cu(In,Ga)SSe₂ (CIGSS) thin films are prepared. Finally, the effective solar cells based on the non-vacuum method in accordance with the invention are also achieved.

The present invention allows the drawbacks of the known non-vacuum techniques to be eliminated. For this purpose, the invention provides a method for preparing CIGSS absorber layers by using a metal salt, thickening and binding agents to form uniform nanoparticle and nanowire networks and to provide a finished high quality CIGSS film after selenization, in which:

a) CIGS nanoparticles and nanowires are produced based on using a metal salt such as metal chloride and acetate at room temperature without inert gas protection;

b) A CIGS precursor layer is coated on a Mo glass substrate by ultrasonic spraying of the CIGS nanoparticle and nanowire solution;

c) Uniform nanoparticle and nanowire networks are generated by initial heat treatment;

d) A clean CIGS precursor layer is obtained by cleaning the residue salts and carbon agents at an increased temperature above 200° C.;

e) High quality CIGSS film is fabricated after selenizing the pretreated precursor layer at a temperature above 500° C.

BRIEF DESCRIPTION OF THE DRAWINGS

According to the following description and drawings of this invention, the objects and features of the present invention will become apparent, which respectively show:

FIG. 1 is a diagram of the fabrication process of CIGS PV device;

FIG. 2 is a diagram of the synthesis process of CIGS nanoparticles/wires;

FIG. 3 is a detailed schematic diagram of the process of preparing CIGSS solar cells based on non-vacuum method.

FIG. 4 is the TEM and the picture of CIGS nanoparticles/wires;

FIG. 5 is the TEM of decomposed CIGS nanowires;

FIG. 6 is a diagram of the selenization temperature profile;

FIG. 7 is cross-sectional TEM of CIGSS films; and

FIG. 8 is the structure diagram and picture of CIGSS device.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

FIG. 1 shows the fabrication process of CIGSS photo-voltaic ("PV") device.

CIGS nanoparticles/wires have been synthesized using the low-cost solution route under atmospheric conditions in accordance with the present invention. The approach is simpler and less costly than any other non-vacuum methods with the following advantages:

(1) Normal atmosphere fabrication. No need to have inert gas protection;

(2) Short reaction time. The whole synthesis process may only take up to 5 minutes;

(3) Formation of amorphous and soluble nanoparticles/wires. The nanoparticles can be deposited on various substrates and turn into uniform thin films at low temperature (<350° C.);

(4) Low cost and easy to scale-up. The amorphous CIGS nanoparticles fabricated in our invention melt under low temperature (even below 180V) and crystallize to various sizes of nanoparticles with increasing temperature (above 200° C.). We observe such dynamical changes by the color of CIGS nanoparticle solutions: with increasing temperature, the color changes from white to red, then to yellow, finally black. We deposit the nanoparticle-based precursor on the Moly-coated substrate, such as a Mo-coated glass substrate, to form a smooth precursor layer. After typical selenization and typical device fabricating process, we obtain high quality CIGSS films and solar cells.

In accordance with the present invention, there is provided a method for preparing effective CIGS-based solar cells, comprising the following steps:

(1) Synthesizing the soluble CuInGaS₂ nanoparticles/nanowires precursor at room temperature under non-vacuum condition. The process of synthesizing CIGS nanoparticles/nanowires, as shown in FIG. 2, includes the following steps:

(a) Providing a solution comprising Cu, In and Ga ions at **26**, **28**, **30**, respectively, in a solvent at **32**, the ratios of Cu, In and Ga ions being in the following proportions: Cu 0.9~1; In 0.6~0.8 and Ga 0.4~0.2 to form the CIG solution at **34**;

(b) Providing a thickening solution at **36**;

(c) Providing a sulfurated precipitant at **38**;

(d) Providing a highly effective coupling agent at **40**;

(e) Adding the solution comprising Cu, In and Ga ions into the thickening solution and stirring the mixture to form homogeneous solution;

(f) Sequentially adding appropriate amount of sulfurated precipitant and coupling agent into above homogeneous solution and stirring the mixture to form a CuInGaS₂ nanoparticles/nanowires well dispersed solution at **42**.

(2) Preparing the CIGS-based ink, adding CIGS powder into specific solvent and adding some additives to form monodispersed CIGS ink. The process of preparing CIGS-based ink includes the following steps:

(a) Separating the CIGS nanoparticles/nanowires by centrifuging method;

(b) Washing and drying the centrifuged CIGS nanoparticles/nanowires under vacuum pump and low temperature;

(c) Providing the high volatilizing solvent with a low boiling point;

(d) Providing a small amount of additives, such as dispersants and thickening agents;

(e) Weighing an appropriate amount of CIGS solid powder, adding into the special organic solvent and some additives, stirring for overnight to form uniform ink.

(3) Ultrasonic spraying CIGS ink on Mo glass substrate, using ultrasonic spray to reduce the aggregation effect of CIGS nanoparticles/nanowires and obtaining uniform CIGS precursor films. The process of ultrasonic spraying CIGS-based ink on Mo-coated glass substrate, such as a glass substrate, includes the following steps illustrated in FIG. 3:

(a) Providing a Mo-coated glass substrate at **44**;

(b) Providing monodisperse CIGS ink at **46**;

(c) Automatically ultrasonic spraying the CIGS ink onto the Mo-glass under 300° C. a plurality of times (e.g. 3 times) at **48**. Using ultrasonic spray technology can effectively reduce the aggregation effect and easily provide uniform and non-aggregated CIGS precursor films.

(4) Heating treatment of the CIGS precursor films at **50**, the soluble CIGS nanopowder will melt again and change to clear solution, as the temperature improve, the uniform and black color CIGS precursor films are obtained after the solution drying.

(5) Selenizing the heat treated CIGS precursor films at **52** t a temperature above 500 C.°, using Se powder as the Se-source and, high quality CIGSS films will be achieved after selenizing the precursor films in the double zonea furnace (e.g. double zone furnace) for approximately one hour. The process of selenization includes the following steps:

(a) Providing pre-treated CIGS precursor films at **54**;

(b) Selenizing the hot-treated precursor films at a temperature above 500 C.° for approximately 30-70 mins in the selenization furnace using Selenium powder as the Se-source, so we can get high-quality CIGSS absorb layer.

Preparing CIGSS device uses typical chemical bath deposition and sputtering and evaporating route. The whole process of fabricating CIGSS PV device includes the following detailed steps:

(a) Depositing buffer layer CdS employing chemical bath deposition ("CBD") method;

(b) Sputtering window layer i-ZnO and conductive AZO layer;

(c) Evaporating Ni/Al top-electrode, at **56**, the standard CIGS PV device with structure of glass/Mo/CIGSS/CdS/i-ZnO/AZO/Ni—Al is obtained in our invention. The detailed schematic diagram of whole process of preparing CIGSS solar cells based on non-vacuum method is shown in FIG. 3.

The typical synthesis of CIGS nanoparticles nanowires-based solution is shown as following:

First, synthesis of CuInGa precursor solution A by: Adding CuCl₂H₂O b (e.g. 0.68 g), InCl₃ (e.g. 0.74 g) and GaCl₃ (e.g. 0.35 g) into 5 mL Methanol, stirring for up to 30 min and a green color solution is obtained.

Second, synthesis of a thickening solution B by: Adding Ethylcellulose (EC) (e.g. 0.3 g) into Terpinol (e.g. 10 mL), stirring overnight and heating to a temperature up to 200° C. until it is completely dissolved.

Then mixing solution A and thickening agent solution B, stirring for up to 5 hours.

Finally, gradually adding Thiourea (e.g. 0.3 g) and 3-MPA (e.g., 2 mL) ("3-Mercaptopropionic Acid") into the mixture of solution A and B and a white nanoparticles-based solution is obtained. The transmission electron microscope ("TEM") and the picture of CIGS nanoparticles and nanowires network are shown in FIG. 4.

The procedures of preparing CIGS ink are described.

First, separating the CIGS nanoparticles/nanowires by methanol using centrifuging method up to five times;

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Second, drying the centrifuged powder under vacuum pump under 100° C. (e.g. 60° C.) for less than 10 hours (e.g. 8 hours), dried powder with a white color is obtained;

Then, weighing the CIGS dried powder (e.g. 3.0 g), adding solvent methyl ethyl ketone ("MEK") (e.g. 70 mL) as the solvent and PEG (e.g. 30 mL) as the thickening agent and sodium hexametaphosphate (SHMP) (e.g. 10 drops) as the dispersant, then mixing together and stirring for overnight to prepare the CIGS ink.

The procedures of ultrasonic spraying CIGS ink are described.

First, providing a clean Mo-coated glass substrate, using acetone, ethanol and DI water to wash the Mo-glass successively, finally using N₂ to blow to dry.

Second, providing monodispersed CIGS ink (e.g. 100 mL) and storing in a bottle, extracting 30 mL ink into a syringe inside which is then ready to spray.

Then, set up the spraying parameters:

Run power of ultrasonic generator: P=less than 15 W (e.g. 5 W);

Temperature of the Mo-glass substrate: T_s=under 300° C. (e.g. 100° C.);

Spraying rate: V=greater than 1 ml/min. (e.g. 3 ml/min.);

Pressure of gas flow: P=greater than 5 Psi (e.g. 15 Psi);

Distance between the nozzle and the Mo-glass substrate: D=less than 150 mm (e.g. 90 mm);

Times of spray: n=less than 5 times (e.g. 3).

Automatically ultrasonic spraying the CIGS ink onto the Mo-glass under 300° C. (e.g. 100° C.) for less than 5 times (e.g. three times). Using ultrasonic spray technology can effectively reduce the aggregation effect and easy to obtain uniform and non-aggregated CIGS precursor films.

The procedures of heating treatment are described. The process of heat treatment includes the following steps:

First, heating the CIGS nanoparticles/nanowires coated substrate up to 350° C. (e.g. 150-200° C.). All the particles are fused and become a clear solution. FIG. 5 shown the nanowires begin to decompose under 150° C.;

Second, heating the sample up to 450° C. (e.g. 250-300° C.). The solution gradually solidified and the color changes from clear to red, finally becoming a deep black. Meanwhile referring to FIG. 5, the networks (on right side of FIG. 5) are formed through the decomposed nanowires (on left side of FIG. 5).

Next the temperature is increased up to 500° C. (e.g. 350° C.) and held for half an hour, which will remove all the organic solvents and additives, finally the color changes to a deep black.

The procedures of selenization process are described.

First, using Selenium powder (e.g. 2.0 g) as the solid-state Se-source and placing it in the graphite box, then placing it into the quartz tube of a selenization furnace at a low temperature zone. The temperature profile of Se-source is shown in FIG. 6;

Second, a sample is placed in the high temperature zone of selenization furnace, then using mixture of Ar or N as the protection gas and Selenizing the hot-treated precursor films above 500° C. (e.g. 550° C.) for 30-70 mins (e.g. 60 mins) in the selenization furnace. FIG. 6 shows the selenization temperature profile.

After selenization, we can get high-quality CIGSS absorb layer, as shown in FIG. 7.

The procedures of fabricating a CIGSS are described.

First, preparing CdS buffer layer through chemical bath deposition (CBD) method:

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Using CdSO₄ (e.g. 0.065 g) and Thiourea (e.g. 1.14 g), adding 25 mL NH₃H₂O and DI water (e.g. 200 mL), stirring and dissolving completely.

Then place the sample into the solution and heat up to 100° C. (e.g. 75° C.) for up to 30 mins (e.g. 15 mins). Taking the sample out and using DI water flushing and removing the aggregated CdS particles. In the end, drying in the oven below 100° C. (e.g. 80° C.) for 60-180 mins (e.g. 120 mins).

Second, sputtering i-ZnO and AZO window layers:

The sputtering depositing parameters of ZnO is shown as following: Sputtering power: P=100-200 W (e.g. 150 W); Sputtering pressure: P=0.5-10 mTorr (e.g. 4.5 mTorr); Ar/O₂=5:1-2:1 (e.g. 3:1); Gas Flow=10-100 sccm (e.g. 25 sccm); Sputtering time: T=up to 20 mins (e.g. 5 mins);

The sputtering depositing parameters of AZO is as following steps: Sputtering power: P=100-200 W (e.g. 150 W); Sputtering pressure: P=3-15 mTorr (e.g. 6.0 mTorr); Gas Flow=10-100 sccm (e.g. 25 sccm); Sputtering time: T=up to 20 mins (e.g. 20 mins).

Finally, evaporating Ni—Al electrode:

Loading Ni wire (e.g. 0.5 g) and Al wire (e.g. 4 g). Sticking the sample with mask covered on the heating stainless steel plate. Sequentially evaporating Ni and Al wires under high vacuum background. FIG. 8 shows the structure diagram and picture of CIGSS device made in accordance with the invention.

The present invention allows the drawbacks of the known non-vacuum techniques to be eliminated. For this purpose, the invention provides a method for preparing CIGSS absorber layers by using a metal salt, thickening and binding agents to form uniform nanoparticle and nanowire networks and to provide a finished high quality CIGSS film after selenization, in which:

a) CIGS nanoparticles and nanowires are produced based on using a metal salt such as metal chloride and acetate at room temperature without inert gas protection;

b) A CIGS precursor layer is coated on a Mo glass substrate by ultrasonic spraying of the CIGS nanoparticle and nanowire solution;

c) Uniform nanoparticle and nanowire networks are generated by initial heat treatment;

d) A clean CIGS precursor layer is obtained by cleaning the residue salts and carbon agents at an increased temperature above 200° C.

e) High quality CIGSS film is fabricated after selenizing the pretreated precursor layer at a temperature above 400° C.

In the process of synthesizing CIGS nanoparticles and nanowires, the steps are performed under ambient condition and room temperature. No inert protection gas and equipments are required in our method and the reaction runs fast and all processes can be finished in a few minutes. No toxic chemicals are involved.

The foregoing is considered as illustrative only of the principles of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention.

What is claimed is:

1. A method of preparing a CIGS-based solar cell comprising the steps of:

synthesizing soluble CuInGaS₂ nanoparticles/nanowires precursor at room temperature under non-vacuum condition by:

preparing a CIGS-based ink, adding CIGS powder into specific solvent and adding additives to form monodispersed CIGS ink;

ultrasonic spraying CIGS ink on Mo-coated substrate, using ultrasonic spray to reduce the aggregation effect of GIGS nanoparticles/nanowires and obtaining uniform CIGS precursor films;

heat treating of the CIGS precursor films to melt soluble CIGS nanopowder and change it to a clear solution, and cooling the solution to dry to a uniform and black color CIGS precursor film;

selenizing the heat treated CIGS precursor films, using Se powder as the Se-source and, creating high quality CIGSS films after selenizing the precursor films in a double zone furnace for approximately 30-70 minutes; and

preparing a CIGSS device by chemical bath deposition and sputtering and evaporating step, wherein said step of synthesizing CIGS nanoparticles/nanowires comprises the steps of:

- providing a solution comprising Cu, In and Ga ions, the ratio of Cu, In and Ga being in the following proportions: Cu 0.9~1; In 0.6~0.8 and Ga 0.4~0.2;
- providing a thickening solution;
- providing a sulfurated precipitant;
- providing an effective coupling agent;
- adding the solution comprising Cu, In and Ga ions into said thickening solution and stirring the mixture to form a homogeneous solution; and
- sequentially adding appropriate amounts of sulfurated precipitant and coupling agent into above homogeneous solution and stirring the mixture to form CuInGaS_2 nanoparticles/nanowires in a well dispersed solution.

2. A method as defined in claim 1, wherein a metal salt is used to produce said nanoparticles and nanowires comprising at least one of a metal chloride and a metal acetate.

3. A method as defined in claim 1, wherein said step of preparing the CIGS-based ink comprises the steps of:

- separating the CIGS nanoparticles/nanowires by centrifuging method;
- washing and drying the centrifuged CIGS nanoparticles/wires under vacuum pump and low temperature;
- providing the high volatilizing solvent with low boiling point;
- providing a small amount of additives, such as dispersants and thickening agents; and
- weighing an appropriate amount of CIGS solid powder, adding into the organic solvent and some additives, stirring for overnight to form a uniform ink.

4. A method as defined in claim 1, wherein said step of ultrasonic spraying CIGS ink on Mo-coated substrate comprises the steps of:

- providing a Mo-coated substrate;
- providing monodisperse CIGS ink; and
- automatically ultrasonically spraying the CIGS ink onto the Mo-coated substrate a plurality of times under 300°C .

5. A method as defined in claim 4, wherein said CIGS ink is sprayed less than five times onto the Mo-coated substrate.

6. A method as defined in claim 1, wherein said selenizing step comprises the steps of:

- providing pre-treated CIGS precursor films; and
- selenizing the hot-treated precursor films at a temperature above 500°C . for approximately 60 minutes in a selenization furnace using Selenium powder as the Se-source to obtain a high-quality CIGSS absorber layer.

7. A method as defined in claim 1, wherein said step of preparing said CIGSS device comprises the steps of:

- depositing a buffer layer of CdS employing CBD method;
- sputtering a window layer of i-ZnO and a conductive AZO layer; and
- evaporating Ni/Al top-electrode to form a CIGSS PV device with structure of glass/Mo/CIGSS/CdS/i-ZnO/AZO/Ni—Al.

8. A method as defined in claim 1, wherein said ultrasonic spraying CIGS ink comprises the steps of:

- providing a clean Mo-coated glass substrate, using acetone, ethanol and DI water to wash the Mo-coated substrate successively, finally using N_2 to blow to dry;
- providing monodispersed CIGS ink and storing in a container, extracting ink for ultrasonic spraying under following conditions or parameters:
 running power of ultrasonic generator: P =less than 15 W;
 temperature of the Mo-coated substrate: T_s =under 300°C .;
 spraying rate: V =greater than 1 ml/min;
 pressure of gas flow: P =greater than 5 Psi;
 distance between the nozzle and the Mo-coated substrate: less than 150 mm;
 number of sprays: n =less than 5 times;
 whereby CIGS ink is ultrasonically sprayed onto the Mo-coated substrate under 300°C . for less than five times, aggregation effect is reduced to obtain uniform and non-aggregated CIGS precursor films.

9. A method as defined in claim 1, wherein said step of selenization comprises the steps of:

- using Se powder as the solid-state Se-source and placing the Se powder in a graphite box, of a low temperature zone of a selenization furnace, heating the Se powder to form Se vapor and carrying the Se vapor through a quartz tube; and
- placing the graphite box in a high temperature zone of the selenization furnace, and then using a mixture of Ar or N as the protection gas.

10. A method as defined in claim 1, wherein the selenization time is approximately 60 mins.

11. A method of preparing a CIGS-based solar cell comprising the steps of:

- synthesizing soluble CuInGaS_2 nanoparticles/nanowires precursor at room temperature under non-vacuum condition by:
- preparing a CIGS-based ink, adding CIGS powder into specific solvent and adding additives to form monodispersed CIGS ink;
- ultrasonic spraying CIGS ink on Mo-coated glass substrate, using ultrasonic spray to reduce the aggregation effect of CIGS nanoparticles/nanowires and obtaining uniform CIGS precursor films;
- heat treating of the CIGS precursor films to melt soluble CIGS nanopowder and change it to a clear solution, and cooling the solution to dry to a uniform and black color CIGS precursor film;
- selenizing the heat treated CIGS precursor films, using Se powder as the Se-source and, creating high quality CIGSS films after selenizing the precursor films in a double zone furnace for approximately 30-70 minutes; and
- preparing a CIGSS device by chemical bath deposition and sputtering and evaporating step, wherein said step of synthesizing CIGS nanoparticles/nanowires based solution comprises the steps of:

- (a) synthesizing a CuInGa precursor solution A by: Adding $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, InCl_3 and GaCl_3 into Methanol, stirring for up to 30 min and a green color solution is obtained;
- (b) synthesizing a thickening solution B by: adding ethyl cellulose (EC) into Terpinol, stirring overnight and heating up to a temperature of 200°C . until it is completely dissolved;
- (c) mixing solution A and thickening agent solution B, and stirring for up to 5 hours; and
- (d) gradually adding Thiourea and 3-MPA into the mixture of solution A and B to obtain a white nanoparticles-based solution.

12. A method of preparing a CIGS-based solar cell comprising the steps of:

synthesizing soluble CuInGaS₂ nanoparticles/nanowires precursor at room temperature under non-vacuum condition by:

preparing a CIGS-based ink, adding CIGS powder into specific solvent and adding additives to form monodispersed CIGS ink;

ultrasonic spraying CIGS ink on Mo-coated glass substrate, using ultrasonic spray to reduce the aggregation effect of CIGS nanoparticles/nanowires and obtaining uniform CIGS precursor films;

heat treating of the CIGS precursor films to melt soluble CIGS nanopowder and change it to a clear solution, and cooling the solution to dry to a uniform and black color CIGS precursor film;

selenizing the heat treated CIGS precursor films, using Se powder as the Se-source and, creating high quality CIGSS films after selenizing the precursor films in a double zone furnace for approximately 30-70 minutes; and

preparing a CIGSS device by chemical bath deposition and sputtering and evaporating step, wherein said step of preparing the CIGS-based ink comprises the steps of:

- (a) separating the CIGS nanoparticles/nanowires by methanol using centrifuging method up to five times;
- (b) drying the centrifuged powder under vacuum pump under 100°C . for less than ten hours to obtain white color dried powder;
- (c) weighing the CIGS dried powder, adding MEK as the solvent and PEG as the thickening agent and SHMP as the dispersant, then mixing together and stirring overnight to form CIGS ink.

13. A method of preparing a CIGS-based solar cell comprising the steps of:

synthesizing soluble CuInGaS₂ nanoparticles/nanowires precursor at room temperature under non-vacuum condition by:

preparing a CIGS-based ink, adding CIGS powder into specific solvent and adding additives to form monodispersed CIGS ink;

ultrasonic spraying CIGS ink on Mo-coated substrate, using ultrasonic spray to reduce the aggregation effect of CIGS nanoparticles/nanowires and obtaining uniform CIGS precursor films;

heat treating of the CIGS precursor films to melt soluble CIGS nanopowder and change it to a clear solution, and cooling the solution to dry to a uniform and black color CIGS precursor film;

selenizing the heat treated CIGS precursor films, using Se powder as the Se-source and, creating high quality

CIGSS films after selenizing the precursor films in a double zone furnace for approximately 30-70 minutes; and

preparing a CIGSS device by chemical bath deposition and sputtering and evaporating step, wherein said heat treatments step comprises:

- (a) heating the CIGSS nanoparticles/nanowires coated substrate up to 350°C . to fuse all the particles to become a clear solution;
- (b) heating the CIGS nanoparticles/nanowires coated substrate up to 450°C . gradually solidify the solution and the color changes from clear to red, and finally becomes deep black and the networks are formed through the decomposed nanowires; and
- (c) increasing the temperature up to 500°C . and holding the temperature for half an hour to remove all the organic solvents and additives to finally cause the color to change to deep black.

14. A method of preparing a CIGS-based solar cell comprising the steps of:

synthesizing soluble CuInGaS₂ nanoparticles/nanowires precursor at room temperature under non-vacuum condition by:

preparing a CIGS-based ink, adding CIGS powder into specific solvent and adding additives to form monodispersed CIGS ink;

ultrasonic spraying GIGS ink on Mo-coated substrate, using ultrasonic spray to reduce the aggregation effect of GIGS nanoparticles/nanowires and obtaining a uniform GIGS precursor film;

heat treating of the GIGS precursor film to melt soluble GIGS nanopowder and change it to a clear solution, and cooling the solution to dry to a uniform and black color GIGS precursor film;

selenizing the heat treated GIGS precursor film, using Se powder as the Se source and, creating high quality CIGSS film after selenizing the precursor film in a double zone furnace for approximately 30-70 minutes; and

preparing a CIGSS device by chemical bath deposition and sputtering and evaporating step, wherein said step of fabricating comprises the steps of:

- (a) preparing a CdS buffer layer through a chemical bath deposition (CBD) method, comprising:
 - (b) using CdSO_4 and Thiourea, adding $\text{NH}_3\text{H}_2\text{O}$ and DI water, stirring and dissolving completely;
 - (c) placing the GIGS precursor film into a solution and heating up to 100°C . for up to 30 minutes and removing the GIGS precursor film and using DI water flushing for removing the aggregated CdS particles and drying in an oven below 100°C . for 60-180 minutes;
- (d) sputtering i-ZnO and AZO window layers,
- (e) the sputtering depositing parameters of ZnO being as follows: sputtering power: P=100-200W; sputtering pressure: P=0.5-10 mTorr; Ar/O₂=5:1-2:1; gas flow=10-100 sccm; sputtering time: T=up to 20 minutes;
- (f) sputtering depositing parameters of AZO being as follows: sputtering power: P=100-200W; gas flow=10-100 sccm; sputtering time: T=up to 30 minutes;
- (g) evaporating Ni—Al electrode comprising:
 - (h) loading NI wire and Al wire and sequentially evaporating Ni and Al wires under high vacuum background to create a CIGSS device.

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